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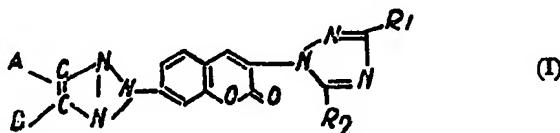
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(54) 3-[1,2,4-TRIAZOLYL-(1)]-7-ARYLTRIAZOLYL-COUMARINES

(71) We, FARBENFABRIKEN BAYER AKTIENGESELLSCHAFT, a body corporate organised under the laws of Germany, of Leverkusen, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

5 This invention comprises new 3-[1,2,4-triazolyl-(1)]-7-aryltriazolyl-coumarine compounds and the production and use of the same as brightening agents.

The new coumarine compounds are of the general formula:—



10 wherein 10
 R₁ and R₂ independently of each other represent hydrogen or optionally substituted, optionally unsaturated alkyl radicals or optionally substituted aryl radicals,

15 A and B together with the carbon atoms to which they are attached form an optionally substituted aromatic-carbocyclic ring free of nitro groups, and the coumarine radical may have further substituents other than any nitro groups. 15

20 When R₁ and/or R₂ represent optionally substituted alkyl radicals, they may represent straight-chain, branched or cyclic, saturated or unsaturated, alkyl groups with 1—12 carbon atoms, which can be substituted by substituents such as halogen atoms, for example fluorine, chlorine and bromine, hydroxyl groups, alkoxy groups with 1—4 carbon atoms, alkyl-carbonyl groups with 1—4 carbon atoms in the alkyl residue, carboxylic acid groups and alkoxy carbonyl groups with 1—4 carbon atoms in the alkyl group, as well as by phenyl radicals which optionally carry halogen atoms, C₁—C₆ alkyl groups and alkoxy groups. 20

25 Suitable alkyl radicals are, for example: methyl, ethyl, β -hydroxyethyl, β -acetoxyethyl, β -chlorethyl, carboxyethyl, carboxethoxyethyl, ethoxyethyl, n- and isopropyl, n-, iso- and tert.-butyl, iso-butenyl, pentyl, hexyl, octyl, decyl, dodecyl, benzyl, p-chlorobenzyl and β -phenylethyl radicals. 25

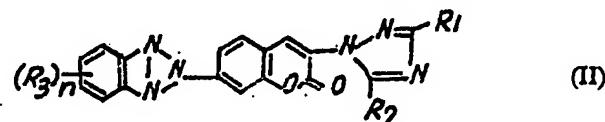
30 When R₁ and/or R₂ are optionally substituted aryl radicals, they are preferably phenyl radicals which can carry one or more substituents, for example fluorine, chlorine, bromine, nitrile and lower alkyl and alkoxy groups with 1—4 carbon atoms. 30

5

A and B together with the carbon atoms to which they are attached in formula (I) preferably form a phenylene, naphthylene or acenaphthylene ring which can optionally be substituted (but not by nitro radicals). Possible substituents, for example, are halogen, nitrile, alkyl, alkoxy, hydroxyalkyl, alkoxyalkoxy, hydroxyalkoxyalkyl, carboxylic acid and sulphonic acid groups or their esters, as well as carbonamide and sulphonamide groups.

5

Preferred compounds are those of general formula:—



10

wherein

R₃ represents a substituent other than a nitro group,
R₁ and R₂ independently of each other represent hydrogen or alkyl groups with 1—4 carbon atoms, and
n is 0, 1 or 2.

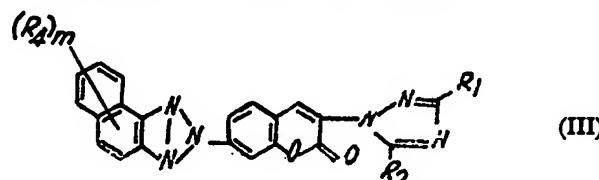
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Of the compounds of formula (II) those which R₃ represents an alkyl or alkoxy group with 1—4 carbon atoms are particularly preferred.

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Further preferred compounds are those of general formula:—



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wherein

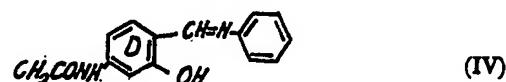
R₄ represents hydrogen or a substituent other than a nitro group,
m is 0, 1 or 2 and

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R₁ and R₂ have the significance indicated in formula (II).

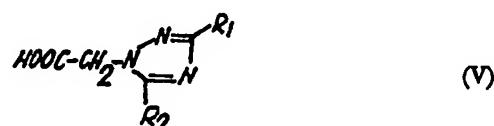
The 3-[1,2,4-triazolyl-(1)]-7-aryltriazolyl-coumarines of formula (I) to be used as brighteners according to the invention are for example obtainable by condensing 4-acetylaminosalicylidene-anilines of formula:—

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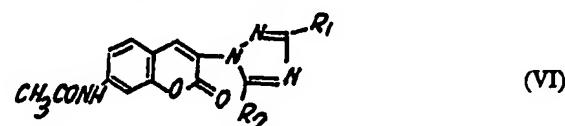
of which the ring D can optionally possess further substituents, with 1,2,4-triazolyl-1-acetic acids of the general formula:—



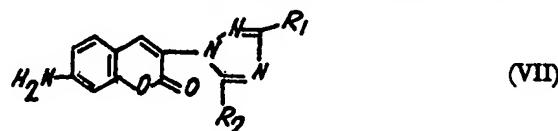
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in which R₁ and R₂ have the abovementioned significance, to give 3-[1,2,4-triazolyl-(1)]-7-acetylaminocoumarines of the general formula:—

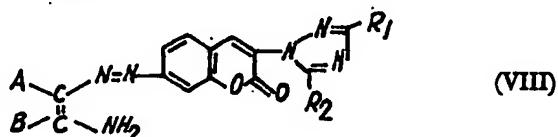
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saponifying the compounds (VI) to give the free amines of the general formula:—



5 diazotising the compounds (VII), reacting the resulting diazonium salts with primary aromatic amines which couple in the *o*-position to the primary amino group, to give 5 *o*-aminoazo compounds of the general formula:—



and triazolising the compounds (VIII).

10 1,2,4-Triazolyl-(1)-acetic acid is known. Corresponding triazolylacetic acids with the substituents R_1 and R_2 can be obtained by reaction of correspondingly substituted 1,2,4-triazoles with halogenacetic esters, for example chloracetic or bromacetic ethyl ester, and subsequent saponification. 10

15 The reaction of the salicylideneanilines (IV) with the triazolylacetic acids (V) takes place in the presence of acid condensation agents, preferably in a mixture of acetic anhydride and sodium acetate, at temperatures of about 140—180°C. The acyl residue is eliminated from (VI) with dilute mineral acids; the subsequent diazotisation is carried out in a known manner in a solution containing mineral acid, as is the coupling to give the compounds (VIII). 15

20 Methods for the triazolisation of the compounds (VIII) to give the compounds of formula (I) are of course well known. It can for example take place by conversion into the copper complexes with copper (II) salts and warming in the presence of excess copper (II) salt. 20

25 The compounds of formula I are suitable for brightening the most diverse materials, above all for brightening fibres, filaments, woven fabrics, knitted fabrics or films of synthetic origin, especially for brightening materials consisting of polyesters in particular aromatic polyesters. They can be employed in the usual manner, for example in the form of aqueous dispersions or in the form of solutions in inert organic solvents; if desired, they can also be used in combination with detergents or added to casting compositions which serve for the manufacture of films or filaments. The amounts of brightening agents required in each case can be easily established by 30 preliminary experiments; in general, amounts of 0.1—1% by weight of brighteners, relative to the weight of the material to be treated, suffice. 30

The parts specified in the examples which follows are parts by weight.

EXAMPLE 1

35 A woven fabric of polyester fibres is padded with an aqueous solution which contains 1 g per litre of 3-[1,2,4-triazolyl-(1)]-7-naphthotriazolyl-coumarine, 2 g of commercially available dispersing agent and 1 g of commercially available wetting agent. The woven fabric is then squeezed out to a weight increase of 100%, and is thereafter dried and heated to 190°C. for 30 seconds. The woven fabric treated in this way shows an intense brightening, of very good light fastness, relative to untreated woven fabric. 35

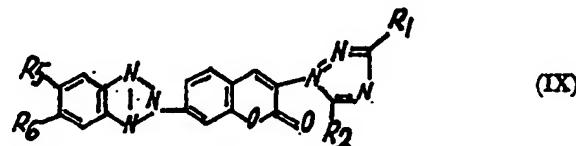
40 The 3-[1,2,4-triazolyl-(1)]-7-naphthotriazolylcoumarine used as the brightener had been manufactured in the following manner:

45 127.6 parts of 4-acetylamino salicylideneaniline, 76.0 parts of 1,2,4-triazolyl-1-acetic acid, 49.0 parts of anhydrous sodium acetate and 255 parts of acetic anhydride were heated for 5 hours under reflux cooling, and whilst stirring 30 parts of the 3-[1,2,4-triazolyl-(1)]-7-acetylamino coumarine thus obtained were then heated for 30 minutes under reflux in a mixture of 220 parts of glacial acetic acid and 50 parts of concentrated hydrochloric acid, and the resulting 3-[1,2,4-triazolyl-(1)]-7-amino-coumarine hydrochloride was diazotised after the reaction solution had cooled to 0—5°C. Thereafter a solution of 14.3 parts of 2-naphthylamine in 20 parts of glacial 50

5 acetic acid was added to the diazonium salt solution whilst stirring; subsequently, the mixture was adjusted to a pH-value of about 4 by dropwise addition of concentrated sodium hydroxide solution and then stirred for a few more hours at room temperature. The resulting azo compound was filtered off, washed with water, dried and suspended in 500 parts of pyridine. The suspension was mixed with 60 parts of copper acetate, heated for 10 minutes to the boil under reflux cooling, and then cooled. The precipitated 3-[1,2,4-triazolyl-(1)]-7-naphthotriazolylcoumarine was filtered off, washed with water and recrystallised from dimethylformamide; it had a melting point of 304—308°C.

10 Instead of the 3-[1,2,4-triazolyl-(1)]-7-naphthotriazolylcoumarine employed in Example 1, it is also possible to use one of the 3-[1,2,4-triazolyl-(1)]-7-aryltriazolylcoumarine compounds listed in the table below as an optical brightener:

TABLE
Compounds of formula:—



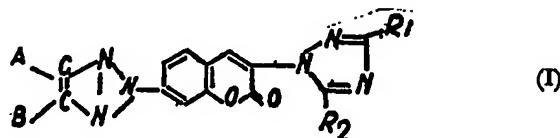
No.	R ₁	R ₂	R ₃	R ₄
1	H	H	CH ₃	OCH ₃
2	H	H	CH ₃	OC ₂ H ₅
3	H	H	CH ₃	OC ₄ H ₉
4	H	H	CH ₃	OCH(CH ₃) ₂
5	H	H	CH ₃	O(CH ₂) ₂ CH ₃
6	H	H	CH ₃	O(CH ₂) ₃ CH ₃
7	H	H	CH ₃	OCH ₂ CH ₂ OC ₂ H ₅
8	H	H	CH ₃	OCH ₂ CH ₂ OH
9	H	H	CH ₃	OCH ₂ CH(CH ₃) OH
10	H	H	CH ₃	OCH ₂ COOH

15 These compounds are obtainable by using the following as coupling components in place of 2-naphthylamine in the method of manufacture indicated in Example 1: 1-methyl-2-methoxy-4-aminobenzene, 1-methyl-2-ethoxy-4-aminobenzene, 1-methyl-2-n-butoxy-4-aminobenzene, 1-methyl-2-i-propoxy-4-amino-benzene, 1-methyl-2-octyloxy-4-aminobenzene, 1-methyl-2-dodecyl-oxy-4-aminobenzene, glycol monoethyl-mono(2-methyl-5-amino)-phenylether, 1-methyl-2-hydroxyethoxy-4-aminobenzene, 1-methyl-2-β-hydroxypropoxy-4-aminobenzene, [2-methyl-5-amino-phenoxy]-acetic acid.

20

WHAT WE CLAIM IS:—

1. 3-[1,2,4-Triazolyl-(1)]-7-aryltriazolyl-coumarine compounds of general formula:—



5 Wherein
 5 R₁ and R₂ independently of each other represent hydrogen or optionally substituted, optionally unsaturated alkyl radicals or optionally substituted aryl radicals, A and B together with the carbon atoms to which they are attached
 10 form an optionally substituted aromatic-carbocyclic ring free of nitro groups,
 10 and
 10 the coumarine radical optionally carries further substituents other than any
 10 nitro groups.

15 2. Coumarine compounds according to claim 1 where R₁ and/or R₂ represent
 15 optionally substituted straight-chain, branched or cyclic, saturated or unsaturated, alkyl
 15 groups with 1—12 carbon atoms.

20 3. Compounds according to claim 2 in which the substituents are halogen atoms,
 20 hydroxyl groups, alkoxy groups with 1—4 carbon atoms, alkylcarbonyl groups with
 20 1—4 carbon atoms in the alkyl radical, carboxylic acid groups, alkoxy carbonyl groups
 20 with 1—4 carbon atoms in the alkyl group or optionally substituted phenyl radicals.

25 4. Compounds according to claim 3 where the phenyl radicals are substituted with
 25 halogen atoms, C₁—C₄ alkyl groups or alkoxy groups.

30 5. Compounds according to any of claims 2, 3 or 4, where the alkyl radicals are
 30 any of those hereinbefore specifically mentioned.

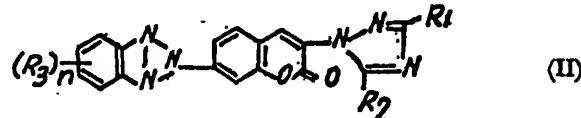
35 6. Compounds according to claim 1 where R₁ and/or R₂ represent a phenyl
 35 radical optionally carrying one or more substituents.

40 7. Compounds according to claim 6 where the substituents are fluorine, chlorine,
 40 bromine, nitrile radicals or lower alkyl or alkoxy groups with 1—4 carbon atoms.

45 8. Compounds according to any of the foregoing claims where A and B together
 45 with the carbon atoms to which they are attached in formula (I) form a phenylene,
 45 naphthylene, or acenaphthylene ring, optionally substituted with groups other than
 45 nitro groups.

50 9. Compound according to claim 8 where the substituents are halogen, nitrile,
 50 alkyl, alkoxy, hydroxylalkyl, alkoxyalkoxy, hydroxylalkoxyalkyl groups, carboxylic acid
 50 or sulphonate acid groups or their esters, carbonamide or sulphonamide groups.

55 10. 3-[1,2,4-Triazolyl-(1)]-7-aryltriazolyl-coumarine compounds according to
 55 either claim 8 or 9 of general formula:—

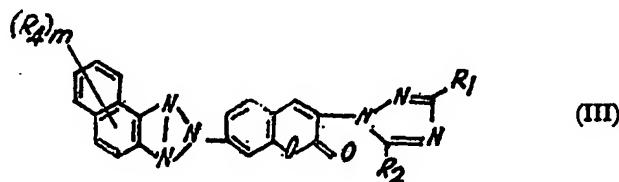


60 wherein
 60 R₁ and R₂ represent hydrogen or alkyl groups with 1—4 carbon atoms
 60 R₃ represents a substituent other than a nitro group, and
 60 n is 0, 1 or 2.

65 11. 3-[1,2,4-Triazolyl-(1)]-7-aryltriazolyl-coumarine compounds according to
 65 claim 10

70 wherein
 70 R₃ represents an alkyl or alkoxy group with 1—4 carbon atoms.

75 12. 3-[1,2,4-Triazolyl-(1)]-7-aryltriazolyl-coumarine compounds according to
 75 either claim 8 or 9 of general formula:—



wherein

R₁ and R₂ represent hydrogen or alkyl groups with 1—4 carbon atoms,
R₄ represents hydrogen or a substituent other than a nitro group, and
m is 0, 1 or 2.

5

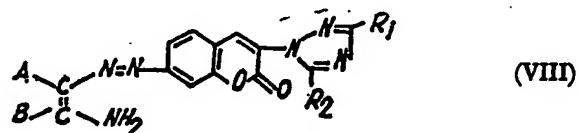
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13. Each of the coumarine compounds according to claim 1 mentioned in Example 1 or 2.

14. Process for the manufacture of 3-[1,2,4-triazolyl-(1)]-7-aryltriazolyl-coumarine compounds according to claim 1 by triazolising o-aminoazo compounds of the general formula:—

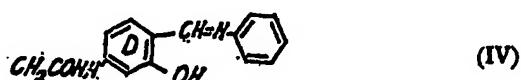
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15. Process according to claim 14 wherein the compound of formula (VIII) is prepared by condensing a compound of the general formula:—

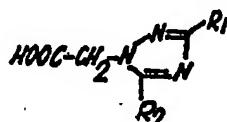
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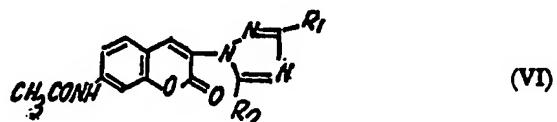
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with a compound of the general formula:—



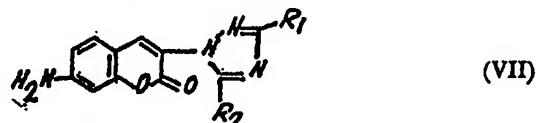
to give a compound of the general formula:—



which is saponified to give a free amine of the general formula

20

20



which is diazotised to form a diazonium salt which is reacted with a primary aromatic amine coupling in the o-position to the primary amino group, whereby the compound of the formula (VIII) is formed.

25

25

16. Process according to claim 14 or 15 when carried out according to Example 1 or 2.

17. Coumarine compounds according to any of claims 1 to 13 when prepared by the process of any of claims 14 to 16.

18. Process for brightening materials by treating the said materials with a dispersion or solution of the coumarine compounds of any of claims 1 to 13 or 17.

5 19. Process according to claim 18 where the coumarine compound is used in an amount of 0.1 to 1% by weight relative to the weight of the material to be treated.

20. Process according to claim 18 or 19 where the material is a synthetic material.

21. Process according to claim 20 where the synthetic material is a polyester fibre.

10 22. Process according to claim 21 where the polyester fibre is fibre of aromatic polyesters.

23. Process according to any of claims 18 to 22 when carried out according to either Example 1 or 2.

15 24. Materials brightened with coumarine compounds by a process according to any of claims 18 to 23.

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